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Nickel catalyzed dealkoxylative C_{sp2}–C_{sp3} cross coupling reactions – stereospecific synthesis of allylsilanes from enol ethers†

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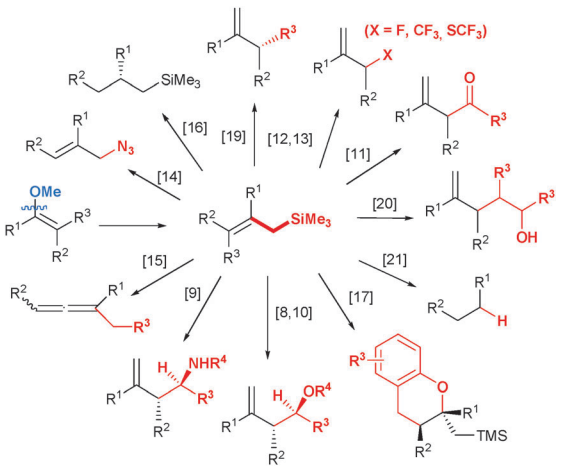
The application of cyclic and acyclic enol ethers as electrophiles in cross coupling reactions offers new possibilities for the preparation of functional compounds. A novel nickel catalyzed dealkoxylative cross coupling reaction allows access to structurally diverse allylsilanes and alcohol derivatives with high stereospecificity and in good yields under mild reaction conditions directly from the corresponding enol ethers.

The development of novel dealkoxylative cross coupling reactions allows the replacement of aryl halides by environmentally friendly and easily accessible anisoles as electrophiles in C_{aryl}–C bond forming reactions.[1] So far the direct arylation with Grignard reagents, boronic esters or organozincates which leads to biaryls,[2] the methylation[3] and the reduction of anisoles in the presence of hydride donors[4] have been reported. However, whereas cross coupling with C_{aryl}–O electrophiles is an emerging field, the potential of enol ethers and O-containing heterocycles as easily accessible, C–O active building blocks in coupling reactions is less explored and limited to the arylation and methylation.[5] Cyclic and acyclic enol ethers can further undergo a wide variety of reactions including β-carbon halogenation, metalation, alkylation, acylation and oxidation, thermal and acid-catalyzed rearrangements, and cycloadditions.[6] Dealkoxylative methods leading to functional building blocks, however, are only known for activated enol phosphates and silyl enol ethers.[7]

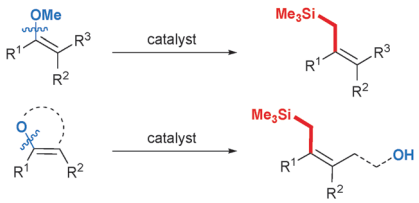
However, if the existing structural variety of enol ethers and oxygen containing heterocycles could be employed in a transformation which leads to allylsilanes, this would be a powerful synthetic tool for the construction of various molecular scaffolds and allow versatile subsequent modifications (Scheme 1).

For the synthesis of a family of bioactive compounds we recently needed a variable stereoselective method for the construction of hydroxyl functionalized allylsilanes. Allylsilanes are widely applied in synthetic chemistry as versatile bench-stable allylation reagents and functional olefins.[8–21] Several methods for their synthesis are known,[22] as they are important building blocks in the syntheses of asymmetric homoallylic alcohols,[8] and amines,[9] ethers,[10] β,γ-unsaturated ketones,[11] allyl fluorides[12] and trimethylfluorides,[13] allyl azides[14] and substituted allenes[15] and form prochiral precursors for TMS functionalized scaffolds[16,17] and polymers[18] (Scheme 1).



Scheme 1 Structural diversity accessible from enol ethers.

In this context, we wondered if readily available enol ethers can be precursors for the synthesis of functionalized allylsilanes and if a metal catalyzed C–O bond cleavage and the new C_{sp2}–C_{sp3} bond formation would proceed stereoselectively (Scheme 2).



Scheme 2 Allylsilanes and allylsilane alcohols *via* C–O bond activation.

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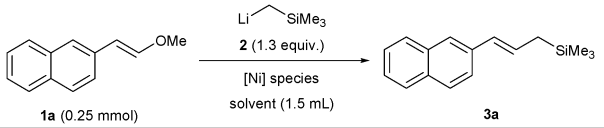
Table 1 Optimization of the dealkoxylating enol ether silylation reaction



Entry	$Ni(COD)_2$ (mol%)	Solvent	Temp. (°C)	Time (h)	Yield[a] (%)	$E:Z$[b]
1	5[c]	Toluene	60	2	82	>20:1
2	5	Toluene	60	2	99	>20:1
3	2.5	Toluene	60	2	97	>20:1
4	—	Toluene	60	2	—	—
5	5	THF	60	2	—	—
6	5	Et_2O	30	2	98	>20:1
7	5	CH_2Cl_2	30	2	—	—
8	5	Toluene	r.t.	2	95	>20:1
9	5	Toluene	60	0.5	90	>20:1

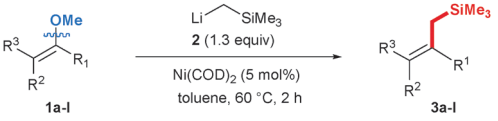
[a] Yield of isolated products. [b] $E:Z$ ratio determined by ^1H NMR. [c] Reaction was performed with 5 mol% $NiCl_2(PPh_3)_2$.

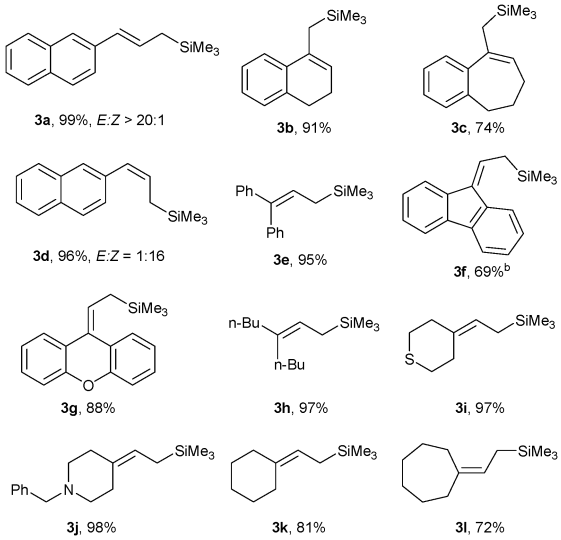
We here report the development of a novel metal catalyzed dealkoxylative C_{sp2}–C_{sp3} cross coupling reaction for the stereoselective preparation of functionalized allylsilanes.[23] These are important intermediates in the synthesis of various chiral heterocycles including substituted oxanes, tetrahydrofuranes, azetidines, pyrrolidines, piperidines and the more complex natural products isoretronecanol and epilupinine.[24]

We started investigating the dealkoxylative cross coupling of enol ethers by reacting (*E*)-2-(2-methoxyvinyl)naphthalene (**1a**) with $LiCH_2SiMe_3$ as the nucleophile in the presence of different catalysts. To our delight, the corresponding *E*-allyltrimethylsilane **3a** was formed with good selectivity ($E:Z > 20:1$) in 82% yield when $NiCl_2(PPh_3)_2$ was applied as the catalyst (Table 1, entry 1). With retaining stereospecificity the yield could be even increased to 99% when $Ni(COD)_2$ (5 mol%) was used as the catalyst (entry 2). Applying 2.5 mol% catalyst led to a slightly lower yield, while no reaction was observed in the absence of a nickel catalyst (entries 3 and 4). Similar good results were obtained in diethyl ether (entry 6), whereas reactions in THF or CH_2Cl_2 did not lead to conversion of starting material (entries 5 and 7). The product was obtained with lower yield, when the reactions were performed at room temperature or with shorter reaction times (entries 8 and 9).

A series of enol ethers was employed to determine the scope of the cross coupling reaction. As shown in Table 2, a wide variety of substrates could be transformed leading to corresponding allyltrimethylsilanes in high yields. The scope includes aromatic (**3a–g**) and aliphatic (**3h–3l**) enol ethers and the reaction proceeded well for double (**3b**, **3c**, **3e–l**) and single substituted double bonds with both retained *E* and retained *Z* configurations (**3a**, **3d**). In addition, enol ethers with nitrogen (**3j**), oxygen (**3g**), and sulfur (**3i**) containing heterocycles reacted under the coupling conditions. Silylenol ethers can be prepared in a simple one-step procedure from ketones and aldehydes[25] and are, therefore, interesting starting materials for the synthesis of allylsilanes.[7] The reaction with silylenol ethers proceeded with similar good yields allowing an extension of the scope to ketone and aldehyde scaffolds (Table 3). Various naphthyl (**1m–n**) and

Table 2 Substrate scope for enol ether substrates[a]





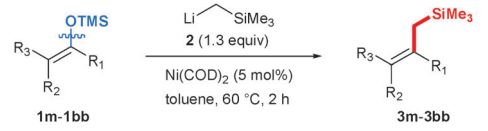
[a] Reaction conditions: 0.25 mmol substrate, 5 mol% $Ni(COD)_2$, 1.3 equiv. $LiCH_2SiMe_3$ in 1.5 mL toluene at 60 °C for 2 h; yields of isolated products are indicated. [b] Room temperature, 0.5 h.

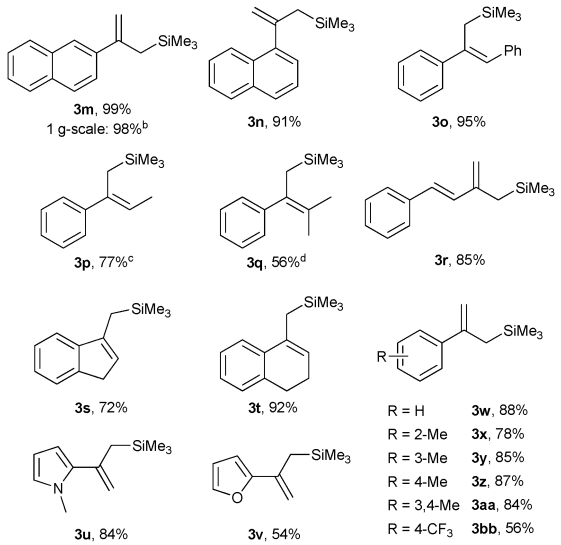
phenyl (**1w–bb**) silylenol ethers reacted smoothly and even allylsilylpyrrole **3u** and furan **3v** were obtained in good yields. To show the applicability, we conducted a scale-up experiment with decreased catalyst loading (1 mol%) and transformed 4.1 mmol of substrate **1m** into 0.97 g (98%) of the corresponding product **3m**. This demonstrates the potential of this methodology.

Given the broad natural availability and structural diversity of heterocycles containing a C_{sp2}–O bond, a ring opening functionalization method with $LiCH_2SiMe_3$ as the nucleophile would allow the preparation of various hydroxyl substituted allylsilanes and phenols, respectively. Due to the structural relation to enol ethers, we chose benzofuran (**4a**) as the first substrate to test our dealkoxylative allysilane formation protocol and obtained 72% of the corresponding phenol substituted product (**5a**) (Table 4, entry 1).

In order to improve the yield and the stereoselectivity, we examined the influence of different ligands on the reaction outcome. Various phosphine ligands (entries 2–8) gave moderate to good yields, with low *Z*-selectivity at room temperature. *E*-Selectivity was only achieved with 40% yield in the presence of traces of THF and PEt_3 as the ligand. However, the more electron rich NHC ligand SIPr·HCl led to 99% yield and 8:1 *Z*-selectivity at room temperature. At −10 °C the stereospecificity was increased to $Z:E = 14:1$ while a slightly lower yield of 93% was obtained (entry 11). Since the yield dropped to 77% with only slightly improved *Z*-selectivity when the temperature was lowered to −25 °C (entry 12), we decided to investigate the scope of the ring opening allylsilylation reaction with the following conditions: $Ni(COD)_2$ and SIPr·HCl at −10 °C with toluene as solvent.

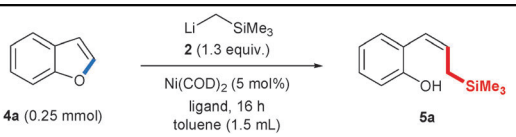
Table 3 Substrate scope for silylenol ether substrates[a]





[a] Reaction conditions: 0.25 mmol substrate, 5 mol% $Ni(COD)_2$, 1.3 equiv. $LiCH_2SiMe_3$ in 1.5 mL toluene at 60 °C for 2 h; yields of isolated products are indicated. [b] Scale-up experiment transforming 4.1 mmol **1m** in 20 mL of toluene, 1 mol% $Ni(COD)_2$. [c] 10 mol% $Ni(COD)_2$, 10 mol% SIPr·HCl. [d] 10 mol% $Ni(COD)_2$, 10 mol% SIPr·HCl, 100 °C.

Table 4 Optimization of the benzofuran ring opening silylation

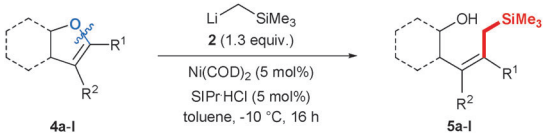


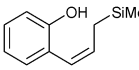
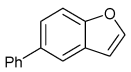
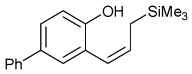
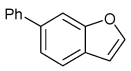
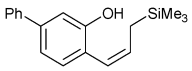
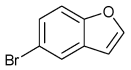
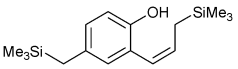
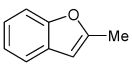
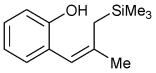
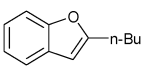
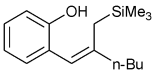
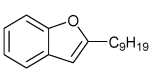
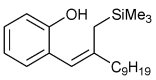
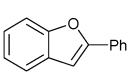
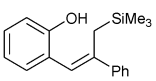
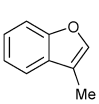
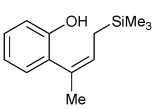
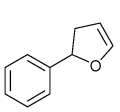
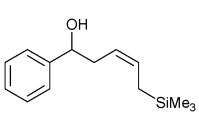
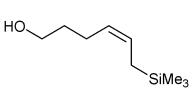
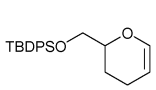
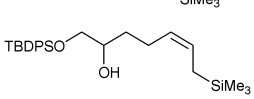
Entry	Ligand (x mol%)	Temp. (°C)	Yield[a] (%)	$Z:E$[b]
1	—	r.t.	72	2.7 : 1
2	PCy_3 (10)	r.t.	93	2.7 : 1
3	PPh_3 (10)	r.t.	91	5 : 1
4	dppe (5)	r.t.	79	3 : 1
5	dppp (5)	r.t.	82	2.7 : 1
6	XANTPHOS (5)	r.t.	73	1.2 : 1
7	TTMPP (10)	r.t.	48	1 : 1.3
8	$P(n\text{-}Bu)_3$ (10)	r.t.	53	1.8 : 1
9	PEt_3 (10, 1 M in THF)	r.t.	40	1 : 16
10	SIPr·HCl (5)	r.t.	99	8 : 1
11	SIPr·HCl (5)	−10	97	13 : 1
12	SIPr·HCl (5)	−25	77	15 : 1

[a] Yield of isolated products. [b] $Z:E$ ratio determined by ^1H NMR.

Various substituted benzofurans, dihydrofurans and dihydropyrans were then applied successfully and the desired products (**5a–l**) were isolated with good yields and high *Z*-selectivities (Table 5). In the presence of 2.5 equiv. of $LiCH_2SiMe_3$, both the $C(sp^2)$–Br and the $C(sp^2)$–O bonds in 5-bromobenzofuran **4d** were cleaved leading to product **5d** which contains both nucleophilic allylsilyl functionality and a $ArCH_2SiMe_3$ moiety suitable for Peterson olefination reactions.[26]

Table 5 Substrate scope of the enol ethers ring opening reaction[a]



Entry	Substrate	Product	Yield (%)	$Z:E$
1			**5a**, 97	13 : 1
2			**5b**, 98	>20 : 1
3			**5c**, 96	>20 : 1
4[b]			**5d**, 91	>20 : 1
5[c]			**5e**, 77	12 : 1
6[c]			**5f**, 82	11 : 1
7[c]			**5g**, 65	10 : 1
8[d]			**5h**, 65	>20 : 1
9[c]			**5i**, 78	9 : 1
10			**5j**, 83	>20 : 1
11			**5k**, 88	>20 : 1
12[e]			**5l**, 63	>20 : 1

[a] Reaction conditions: 0.25 mmol substrate, 5 mol% $Ni(COD)_2$, and 1.3 equiv. $LiCH_2SiMe_3$ in 1.5 mL toluene at −10 °C for 16 h; yields of isolated products are indicated. [b] 2.5 equiv. $LiCH_2SiMe_3$. [c] 60 °C, 2 h. [d] 10 mol% $Ni(COD)_2$, 10 mol% SIPr·HCl, 80 °C, 2 h. [e] 10 mol% $Ni(COD)_2$, 10 mol% SIPr·HCl.

In addition to aromatic substituted allylsilanes, we were able to synthesize primary and secondary alcohols *via* opening of substituted and unsubstituted furan and pyran ring systems. The cleavage of 2-phenyl-2,3-dihydrofuran (**4j**) led to the homoallylic alcohol (**5j**). In addition, alcohol **5k** was obtained by the Ni-catalyzed allylsilylation of 3,4-dihydro-2*H*-pyran with high stereoselectivity ($Z:E$ > 20 : 1). Tolerating TBDPS protecting groups our method is further suitable to synthesize monoprotected diols with allylsilyl functionality (**5l**).

In summary, we have developed a metal-catalyzed dealkoxylative C_{sp2}–C_{sp3} cross-coupling reaction of cyclic and acyclic enol ethers. Applying a readily available nickel catalyst and nucleophile, various allylsilanes, important building blocks in synthetic chemistry, were prepared under mild reaction conditions with good yields and high stereospecificity. The reaction can be performed at a larger scale with lower catalyst loadings. Compared to other allylsilane syntheses, the described cross coupling stands out due to the wide substrate scope, the accessibility of substrates and the practicality allowing the stereoselective product formation under mild reaction conditions even on a larger scale. In fact the allylsilanes described here are not easily prepared using alternative methodology and, therefore, the procedure should be of interest. Further studies on dealkoxylative cross couplings and their synthetic applications are currently underway in our group.

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